PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A23B 7/00, B65D 51/16

A1

(11) International Publication Number: WO 94/12040

(43) International Publication Date: 9 June 1994 (09.06.94)

(21) International Application Number: PCT/US93/10669

(22) International Filing Date: 3 November 1993 (03.11.93)

(30) Priority Data:
07/981,160 24 November 1992 (24.11.92) US

(71) Applicant: FRESH WESTERN MARKETING, INC. [US/US]; 1156 Abbott Street, Salinas, CA 93901 (US).

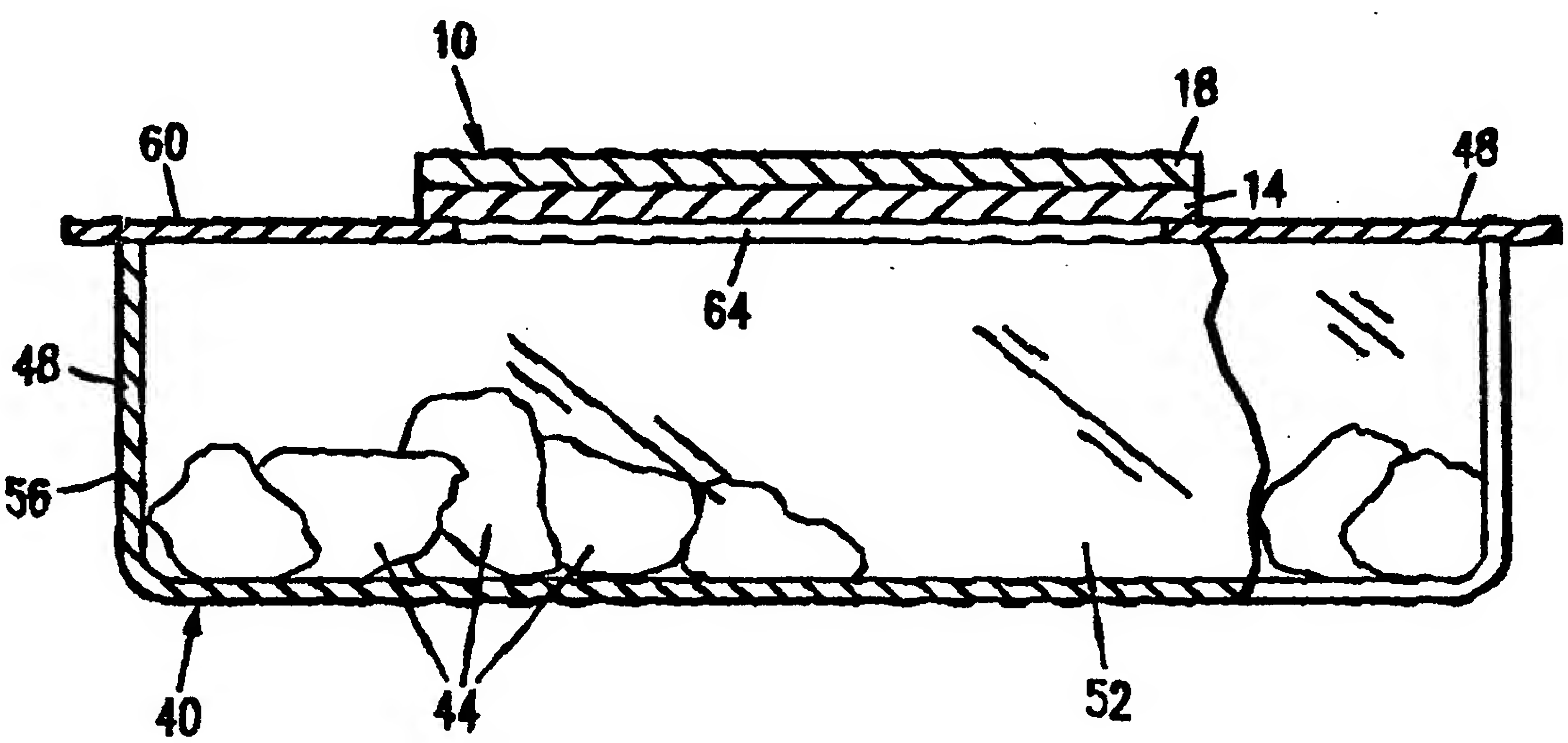
(72) Inventors: VARRIANO-MARSTON, Elizabeth; 2011 Foulk Road, Wilmington, DE 19810 (US). THOMAS, Eugene, P.; 1809 Via Pacifica, Aptos, CA 95003 (US). ANTOON, Mitchell, K., Jr.; 4013 Country Village Drive, Raleigh, NC 27606 (US).

(74) Agents: LaRIVIERE, F., David et al.; LaRivière & Grubman, Two Harris Court, Suite A2, Monterey, CA 93940 (US).

(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: COATED MEMBRANE FOR CONTROLLED ATMOSPHERE PACKAGE



(57) Abstract

A coated membrane (10) for use in controlling the oxygen and carbon dioxide ratio inside of a package (40) that holds respiring produce (44) such as fruits, vegetables or flowers. The coated membrane comprises a porous substrate (14), such as a polypropylene film, and has an oxygen permeance in the range of 5,000 to 30,000,000 cc/100 sq. in-atmosphere-day. The substrate is coated with a material that is substantially impermeable to oxygen, such as an acrylic emulsion, so that the amount of substrate surface area covered with the coating causes a decrease in the oxygen permeance of the substrate. The coating is applied to the substrate using a flexographic or rotogravure or rotary silkscreen process.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

PATENT APPLICATION

COATED MEMBRANE FOR CONTROLLED ATMOSPHERE PACKAGE

COATED MEMBRANE FOR CONTROLLED ATMOSPHERE PACKAGE

TECHNICAL FIELD

This invention relates to the field of packaging for respiring items such as fresh fruits and vegetables and more particularly to a coated porous membrane for use in controlling the flow of oxygen and carbon dioxide into and/or out of a produce container.

BACKGROUND ART

It is well-known that the eating qualities and/or appearance of respiring items such as fresh fruits, vegetables and flowers (hereinafter "produce") can be preserved by controlling the atmosphere inside of the package that holds the produce. For example, U.S. Pat. No. 4,842,875, issued to H. Anderson on June 27, 1989, describes a basic approach that involves controlling the flow of oxygen and carbon dioxide into and out of the container that holds the produce. The container, called a "controlled atmosphere package," is comprised of a substantially gas-impermeable package having one or more panels made of a microporous plastic membrane having an oxygen permeance in the range of 77,500 to 465,000,000 cc/m^2-atmosphere-day. By varying the permeance and/or size of the panel, various optimized oxygen and carbon dioxide levels inside the package can be maintained for extended periods of time thereby providing a method for retarding the maturation processes of various produce commodities.

U.S. Pat. No. 4,923,703, issued to M. Antoon on May 8, 1990, describes a microporous film for use as a panel in a controlled atmosphere package, comprised of a uniaxially oriented polyolefin film with an inert filler.

U.S. Pat. No. 4,910,032, issued to M. Antoon on March 20, 1990, describes a controlled atmosphere package, having a first membrane comprised of a uniaxially or biaxially oriented polymer film that is permeable to oxygen and carbon dioxide, and a second membrane that is permeable to water but impermeable to oxygen and carbon dioxide.

U.S. Pat. No. 4,879,078, issued to M. Antoon on November 7, 1989, and U.S. Pat. No. 4,923,650, issued to M. Antoon on May 8, 1990 describe methods for preparing microporous films that can be used in controlled atmosphere packaging for produce.

Additional patents that deal with this field include U.S. Pat. No. 4,939,030, issued to S. Tsuji et al. on July 3, 1990, which discloses a three-layer film, including a vinyl acetate layer, for use in produce packaging; and U.S. Pat. No. 4,996,071, issued to L. Bell on February 26, 1991, which discloses varying the surface area of the film to control the atmosphere inside of a produce package.

Additional patents dealing with this field but which are not considered to be material to the present invention include U.S. Pat. No. 3,625,876, issued to C. Fitko on December 7, 1971; U.S. Pat. No. 4,769,262, issued to A. Ferrar et al. on September 6, 1988; and U.S. Pat. No. 5,026,591, issued to R. Henn et al. on June 25, 1991.

All of this prior art teaches that in order to establish and maintain different oxygen/carbon dioxide ratios inside of the package, either the permeance of the microporous membrane must be changed by altering the chemical formulation of the film used to make the membrane, or the size of the membrane panel must be changed.

DISCLOSURE OF INVENTION

The present invention comprises a coated porous membrane panel for use with a container that holds produce. The coated porous membrane panel is positioned in contact with, and over a hole in, a substantially non-porous container for providing an area through which a limited volume of carbon dioxide and oxygen can flow at

a rate (permeance) between the inside of the container and the outside ambient atmosphere which is within a range specific to the type and amount of produce in the package. The combination of the non-porous container and the coated porous membrane panel retards the maturation of the produce by allowing the concentration of oxygen and carbon dioxide inside the container within a rang of concentration reasonably optimal for the type and amount of produce within the package. The coated porous membrane panel of the present invention may be comprised of a base substrate such as polypropylene or polyethylene, a nonwoven substrate made from these polymers, or paper (hereinafter "substrate") which has a permeance rate to oxygen and carbon dioxide in a range of, for example, 77,500 to 465,000,000 cc/m^2-atmosphere-day (5,000 to 30,000,000 cc/100 in^2-atmosphere-day). This range is then reduced to a desired level suitable for the type and amount of produce to be packaged by applying to said substrate a coating of a porosity-reducing, film-forming substance, such as an acrylic-based polymer, which by is coat weight (thickness) and/or pattern of application, decreases the permeance rate of the substrate to a desired range of permeance rates. The percent reduction in the oxygen and carbon dioxide permeance rate of the substrate can be varied 15 percent to almost 100 percent by varying the aforementioned characteristics of the coating applied to it.

The coated porous membrane panel of the present invention differs from the porous membrane panel described in the prior art (e.g., by Antoon in U.S. Pat. No. 4,879,078) in that the prior art varies the constituents of the membrane material to produce membranes of varying permeances, whereas in the present invention, a single substrate can be used to produce difference membranes for different types and/or amounts of produce by simply varying the characteristics of a porosity-reducing coating material applied to the single substrate.

BRIEF DESCRIPTION OF DRAWINGS

For fuller understanding of the present invention, reference is made to the accompanying drawing in the following Best Mode of Carrying Out the Invention. In the drawing:

Figure 1 is a schematic cross-sectional representation of a coated membrane according to the present invention.

Figure 2 is a top view of a membrane having the coating applied in a triangular pattern.

Figure 3 is a top view of a membrane having the coating applied as a solid pattern.

Figure 4 is a cross-sectional view of a container according to the present invention.

Figure 5 is a schematic cross-sectional representation of a coated membrane having an ink layer and an adhesive layer.

Reference numbers refer to the same or equivalent parts of the present invention throughout the several figures of the drawing.

BEST MODE OF CARRYING OUT THE INVENTION

Fig. 1 is a schematic illustration of a coated membrane 10 according to the present invention. The membrane 10 comprises a substrate 14 and a coating 18 that is applied to a surface 16 of the substrate 14 to decrease the permeance of substrate 14 to oxygen and carbon dioxide. The surface 16 is a face of the substrate 14 through which oxygen and carbon dioxide must pass in order to flow through the substrate 14.

The substrate 14 may be any porous material having the following characteristics: (1) the permeability to oxygen should be in the range of 77,500 to 465,000,000 cc/m^2-atmosphere-day (5,000 to 30,000,000 cc/100 in^2-atmosphere-day); (2) the substrate 14 must be compatible with the coating 18, with an adhesive and with printing ink; and (3) the CO_2/O_2 permeance ratio of the substrate 14 can range from 1:1 to 8:1 with the preferred range being 1:1 to 4:1.

In the preferred embodiment, the substrate 14 is a microporous polypropylene film such as the film described by Antoon in U.S. Pat. No. 4,879,078 (i.e., comprised of a uniaxially oriented film comprised of a blend of 36% to 60% by weight of propylene homopolymer or propylene/ethylene copolymer, 36% to 60% of calcium carbonate filler based on the total weight of the polymer and filler, 0.10-2.5% by weight of calcium stearate, and 0-1.5% by weight of stabilizer). Although there is no preferred shape or size for the membrane 10, for reference purposes only, the substrate 14 typically has a length "L" in the range of 1.0 to 4 inches and a thickness "t" in the range of 5.0 to 10.0 mil. In general, any of the polymers

described by Antoon in U.S. Pat. No. 4,879,078 can be used as the substrate 14, including the polyolefin homopolymers described therein.

Numerous other materials having the characteristics listed above may be used as the substrate 14, including the microporous polymer films described by Anderson in U.S. Pat. No. 4,842,875 that utilize a variety of inorganic fillers such as clay, barium sulfate, calcium carbonate, silica, diatomaceous earth and titania, and those using organic polymer fillers such as polyesters, polyamides and polystyrene.

It has also been observed that the substrate 14 may be comprised of a coated or uncoated paper having a weight in the range of 55 lbs. to 110 lbs. (e.g. the TEXAPRINT brand paper or white C1S latex impregnated paper manufactured by Kimberly-Clark). The clay coated paper should also have the permeance and compatibility characteristics listed above.

The coating 18 used on porous substrate 14 may be any material that substantially reduces the permeance of the substrate 14 to oxygen and carbon dioxide. Such materials are typically referred to as "barrier coatings" and include acrylic emulsion polymers, polyvinyl acetate homopolymer emulsions, and nitrocellulose polymers. For practical reasons, other desirable characteristics for the coating 18 include: water resistance, FDA approval for indirect food contact, and good film forming qualities, namely the ability to form a continuous barrier coating 18 that can be applied to the substrate 14 without the formation of pin holes.

In the preferred embodiment, the coating 18 comprises an acrylic based polymer supplied by Johnson & Johnson under the trademark JONCYRYL 74F. ICI also markets an acceptable acrylic based polymer under the trademark NeoCryl® which may be used as the coating 18. For reference purposes, the coating 18 generally has a coatweight of about 45% (i.e. about 45% by weight of solids), and a thickness "f" of about 0.25 to 0.5 mil. When paper is used as the substrate, porosity-reducing coating layer 18 may consist of the ink used to print information on the paper (i.e., experiments have shown that 80-lb clay-coated paper, for example, absorbs sufficient ink to reduce the permeance of the paper approximately 70%). The coating 18 may be applied to the substrate 14 in-line during a label making process, or the substrate 14 may be coated off-line using standard printing processes.

In the label manufacturing process, a roll of substrate material is converted to pressure-sensitive adhesive labels. The conversion process involves running a roll of substrate material through a label manufacturer's printing press where the substrate material's top surface is printed with inks, the perimeter of the back surface is coated with adhesive, the labels are die-cut into desired label shapes, and the resulting master roll of labels is slit and wound into individual rolls of labels that are dispensed onto packages by the food packer.

Flexography is a widely used process for printing roll-fed pressure sensitive, self-adhesive labels. Flexography is a relief-printing technique. The first step is to make a flexible printing plate of rubber or plastic, with the print image area of the plate raised above the nonimage areas. The flexible plate is wrapped around a cylinder and placed in one of several printing stations of a flexographic press. Ink rollers on the press touch only the top surface of the raised image area of the flexo plate, and ink is transferred directly from the image areas of the plate to the substrate to be printed. After applying the ink to the top surface of the substrate, adhesive is applied to the back surface, and the labels are passed through a drying station, a die cutting station, and wound onto a take-up roll.

Flexographic printing processes and gravure printing processes are described in the book "Printing Ink Handbook" compiled by Product and Technical Publications Committee, National Association of Printing Ink Manufacturers, Inc, 1976.

Fig. 2 illustrates a top view of the coated membrane 10 in which the coating 18 is applied as a repeating pattern of triangles using the flexographic process. In Fig. 2, the dark triangles 24 represent areas to which the coating 18 has been applied, while the light triangles 28 represent areas to which no coating has been applied. Therefore, the light triangles 28 represent the exposed surface 16 of the substrate 14.

Similarly, in Fig. 3 the coating 18 is represented by a dark area 32 and the exposed surface 16 of the substrate 14 is represented by the light area 36.

The coating patterns illustrated in Figs. 2 and 3 are illustrative of a virtually unlimited number of possible coating patterns. Any pattern that decreases the uncoated, permeable area of the substrate 14 is acceptable for use in the present invention.

Fig. 4 illustrates a rigid container 40 for holding respiring produce 44. The term "respiring items" means items that respire in the biochemical sense of the word (i.e. that take in oxygen and give off carbon dioxide). The container 40 is comprised of a substantially impermeable packaging material 48 that surrounds the produce and holds it in a chamber 52 formed by the packaging material 48. The container 40 thus prevents any appreciable exchange of oxygen or carbon dioxide from within or outside container 40 except through the membrane 10.

In the preferred embodiment, the packaging material 48 is approximately 15-20 mil thick PVC. However, as is described in U.S. Pat. No. 4,842,875, any substantially impermeable material suitable for packaging produce, like glass, metal or a wide range of plastics (e.g. polyolefins and polystyrene) can be used for the packaging material 48. The term substantially impermeable is defined in U.S. Pat. No. 4,842,875 and means that no appreciable amount of oxygen can pass through the packaging material 48.

In Fig. 4, the container 40 is shown as having the shape of a basket with a bottom part 56 and a top part 60 that fit tightly together in a gas-tight manner. However, it should be appreciated that the container 40 can take other forms, such as a 3 mil thick polyethylene bag, having a 4.0% ethylene/vinylacetate content. The only requirements for the container 40 is that it be comprised of the substantially impermeable packaging material 48 and that it surround and hold the produce 44 in a chamber 52 so that the only passageway for oxygen to reach or leave the chamber 52 is through the membrane 10.

An aperture 64 exists in the container 40. The aperture 64 is an open region (hole) in the container 40 not covered by the packaging material 48. The membrane 10 is positioned over or about the aperture 64 so as to prevent gasses such as oxygen and carbon dioxide from passing between the chamber 52 and the ambient atmosphere without passing through the membrane 10.

Fig. 5 illustrates a membrane 70 in which an ink layer 74 has been printed on top of the coating 18. The ink layer 74 is comprised of ink, water-based or otherwise, that is permeable to oxygen and carbon dioxide and functions merely to convey printed information, such as information about the produce 44, to the consumer. It should be appreciated that the relative positions of the substrate 14, the

coating 18 and the ink layer 74 are not important. The ink layer 74 could be located between the substrate 14 and the coating 18 provided that coating 18 is transparent. Similarly, the ink layer 74 and the coating 18 could be on opposite sides of the substrate 14.

An adhesive 78 has been applied to the side of the substrate 14 not containing the ink layer 74. The finished label adhesive thickness "d" should be about 1.5 mil ± .3 mil. The primary function of the adhesive 78 is to attach the substrate 14 to the packaging material 48. Any pressure-sensitive label adhesive that is approved for indirect food contact can be used as the adhesive 78.

As is shown in Fig. 5, generally the adhesive 78 is applied around the outer edges of the substrate 14 so as to leave a region 82 on the substrate 14 that is not covered with adhesive 78. Since the adhesive areas 78 are attached to the packaging material 48, the part of the membrane 10 that is "over" the adhesive areas 78 is effectively impermeable to oxygen and carbon dioxide. Thus, only the part of the membrane 10 that is "over" the region 82 is a "breathable" area through which oxygen and carbon dioxide can pass.

Referring to Figs. 1-5, the functioning of the present invention can now be explained. The coating 18 is applied to the substrate 14 to decrease the permeance of substrate 14. In theory, for a substrate 14 having a fixed surface area, the permeance can be decreased by any amount between 0 and 100% by applying the coating 18 to an appropriate area of the substrate 14. It is thought that the coating 18 reduces the permeance of the substrate 14 by blocking the pores that exist in the substrate 14 that provide passageways for the flow of oxygen or carbon dioxide through the substrate 14.

By applying the coating 18 to the substrate 14 in a pattern that covers less than an entire surface of the substrate 14, the permeance of the substrate 14 can be reduced by a value less than 100%. For example, in Fig. 2, the dark triangles 24 cover approximately 80% of the surface area of the substrate 14 and therefore are expected to

decrease the oxygen permeance by about 80%. Similarly, in Fig. 3, if the coating 18 covers about 50% of the surface area of the substrate 14, as represented by the dark area 32, then it is expected that the oxygen permeance of the coated membrane shown in Fig. 3 would be reduced by 50% compared to the permeance of the uncoated substrate 14.

In practice, a one-to-one relationship between the surface area coated and the reduction in effective permeance is not observed. Generally, the observed reduction in effective permeance is somewhat less than would be expected if the coating was a perfectly effective pore blocker. For example, in Example 1 (below), when a 50% pattern was used, a 31% decrease in permeance was observed.

A major advantage of the present invention is that by using patterns of differing surface areas, a single substrate 14, having a fixed oxygen permeance, can be used to prepare a variety of membranes 10 that have different permeances after the coating 18 is applied in different patterns and different coating weights and formulations. This is useful because in order to optimize the storage life of different types of produce 44, membranes 10 of varying oxygen permeance are required.

In the preferred embodiment, the coating 18 is applied to the substrate 14 using a flexographic process. In the flexographic process, a flexible rubber or plastic plate ("Flexo Plate") is made having an image of the coating pattern which is to be transferred to the substrate 14 (e.g. the patterns shown in Figs. 2 and 3). During the conversion, the coating material is transferred from the raised or image areas of the Flexo Plate to the substrate in the desired pattern.

In order to obtain reproducible results from run to run using the flexographic process, parameters such as the following should be controlled (the listed parameter values were selected as optimal for the particular flexographic system used with the present invention):

1. The actual temperatures of the drier and adhesive should be

maintained at a constant value (ink drying - 150 °F; adhesive pan temperature - 340 °F); 2. The viscosity of the coating should be maintained at a constant value (generally about 200-250 cp); 3. The Flexo Plate to substrate pressure should be uniform and the Flexo Plate should be cleaned periodically during the run; 4. The run speed should be maintained at a constant value (generally about 40 ft./min.); and 5. The analox roll should be cleaned periodically during the run - typically, about every 1000 impressions (a 300 line analox roll with a doctor blade has been used for all coating runs).

While the flexographic process is the presently preferred method of producing the membranes 10, it should be appreciated that any method of applying a coating to a substrate could be used, including rotogravure processes, letter press processes and rotary silkscreen processes.

EXAMPLE 1

A roll of microporous polypropylene film obtained from Hercules, Inc., a calcium carbonate-filled uniaxially oriented polypropylene film having an oxygen permeance of approximately 565,000 cc/100 in^2-atmosphere-day, was loaded onto the printing press and the following operations were performed on the press: 1. An acrylic coating (JONCYRYL 74F), having a proprietary chemical composition, was applied to the film (a copolymer substrate), using a flexographic plate; 2. Graphics and text were printed over the acrylic coating; 3. The adhesive was pattern-applied to the back surface of the substrate; 4. The coatings were dried in an oven at 150 degrees F; and 5. The labels were die-cut to the desired shape. This process was repeated a number of times using flexographic plates containing patterns for applying the acrylic coating to 25%, 50%, 75%, 90% and 100% of the surface area of the substrate label. The permeance of the various labels was measured using an oxygen permeance tester and the following data were obtained (permeance values are in units of cc/100 in^2-atmosphere-day):

Sample	Permeance* Range (x 1000)	Permeance* (mean ±std) (x 1000)	Average % Perm. Red.
Unconverted Film	542-573	565 ±13	--
Converted Film	517-540	529 ±10	6%
25% Coating Coverage	428-480	461 ±24	18%
50% Coating Coverage	354-432	388 ±38	31%
75% Coating Coverage	265-394	336 ±49	41%
90% Coating Coverage	63-113	78 ±23	86%
100% Coating Coverage	12-62	44 ±20	92%

* In units of cc/100 in^2-atm-day.

TABLE 1.

EXAMPLE 2

A roll of microporous polypropylene film obtained from Hercules, Inc., a calcium carbonate-filled uniaxially oriented polypropylene film (a copolymer substrate) having an oxygen permeance of approximately 477,000 cc/100 in^2-atmosphere-day, was converted into acrylic-coated (JONCYRYL 74F) membrane labels as described in Example 1. However, the viscosity of the coating was varied as indicated in Table 2 by changing the ratio of acrylic emulsion to water in the coating mixture.

Examination of the data in Table 2 shows that the average reduction in permeance is dependent on the viscosity of the coating 18 so that this parameter may be controlled in order to achieve reproducible results.

Sample	Permeance* Range (x 1000)	Permeance* (mean ±std) (x 1000)	Average % Perm. Red.
Unconverted Film	455-498	477 ±19	--
50% Coating Coverage; Viscosity = 200-250 cp	263-329	299 ±22	37%
50% Coating Coverage; Viscosity = 400 cp	191-220	210 ±15	56%
75% Coating Coverage; Viscosity = 200-250 cp	120-195	158 ±22	67%
75% Coating Coverage; Viscosity = 390 cp	172-218	196 ±15	59%

* In units of cc/100 in^2-atm-day.

TABLE 2.

EXAMPLE 3

A roll of microporous polypropylene film obtained from Hercules, Inc., a calcium carbonate-filled uniaxially oriented polypropylene film (a copolymer substrate) having an oxygen permeance of approximately 567,000 cc/100 in^2-atmosphere-day, was loaded onto a Dikon coater and the following operations were performed in succession on the coater: (1) an acrylic coating (NeoCryl®), having a solids content of 25%, was applied to the surface of the film substrate using a trihelicoid gravure cylinder (180 cells/linear inch), (2) the film was passed through a 140 degrees F oven at a speed of 40 ft/min to dry the coating, and (3) the coated film was wound onto a take up roll. This process was repeated with a second roll of microporous film having an oxygen permeance of 548,000 cc/100 in^2-atmosphere-day.

The data in Table 3 shows that the gravure printing method reduced the permeance of the films by approximately 41 to 48 percent.

Film Samples	Uncoated Film Permeance* (x 1000)	Gravure-Coated Film Permeance* (x 1000) (mean ± std)	Average Perm. Red.
6-175-01-00640-0608-58	567	294 ± 39	48.2%
6-175-01-00640-0608-64	548	323 ± 53	41.1%

* In units of cc/100 in^2-atm-day.

TABLE 3.

It should be noted that, while the conversion process of the present invention is described as a sequence of applying coating layers, the order of applying the layers is unimportant. It should also be noted that typically each layer must be allowed to dry before the next layer is applied.

The present invention has been particularly shown and described with respect to certain preferred embodiments of features thereof. However, it should be readily apparent to those of ordinary skill in the art that various changes and modifications in form and details may be made without departing from the spirit and scope of the invention as set forth in the appended claims.

CLAIMS

We claim:

1. A membrane for regulating the ratio of oxygen and carbon dioxide inside of a container that holds respiring items comprising:

a substrate having a permeance to oxygen in the range of approximately 5,000 to 30,000,000 cc/100 in^2-atmosphere-day; and

a coating applied to a surface of the substrate for reducing said permeance to oxygen by between fifteen and ninety percent.

2. The membrane of claim 1 wherein the substrate comprises a polymeric film.

3. The membrane of claim 1 wherein the substrate comprises a polypropylene film.

4. The membrane of claim 1 wherein the substrate comprises a calcium carbonate-filled uniaxially oriented polymer film comprised of approximately 36% to 60% by weight of polyolefin polymer and 36% to 60% by weight of calcium carbonate, based on the weight of the polymer and calcium carbonate.

5. The membrane of claim 1 wherein the coating comprises an acrylic polymer.

6. The membrane of claim 1 wherein the coating is selected from the group consisting of acrylic polymers, polyvinylacetate or nitrocellulose.

7. The membrane of claim 1 wherein the coating is applied to the substrate using a flexographic process.

8. A membrane for regulating the concentration of oxygen and carbon dioxide inside of a container that holds fresh fruit, vegetables or flowers comprising:

a substrate comprised of a polypropylene film having a permeance to oxygen in the range of approximately 5,000 to 30,000,000 cc/100 in^2-atmosphere-day; and

a coating comprised of an acrylic based polymer applied to a surface of the substrate for reducing said permeance to oxygen by between fifteen and ninety percent.

9. The membrane of claim 8 wherein the coating is applied to the substrate using a flexographic process.

10. A container for retarding the maturation of respiring items comprising:

package means for substantially surrounding a respiring item and holding the respiring item in an internal chamber formed by the package means, the package means being comprised of a material that is essentially impermeable to oxygen and carbon dioxide;

at least one panel means for providing a limited flow of carbon dioxide and oxygen between said internal chamber and the ambient atmosphere, the panel means being positioned in contact with said package means and having a permeance to oxygen in the range of approximately 5,000 to 30,000,000 cc/100 in^2-atmosphere-day; and

a coating means applied to said panel means for decreasing the permeance of said panel means to oxygen or carbon dioxide by more than fifteen percent.

11. The container of claim 10 wherein the package means comprises a polymeric container.

12. The container of claim 10 wherein the package means comprises a PVC container.

13. The container of claim 10 wherein the panel means comprises a polymeric film.

14. The container of claim 10 wherein the panel means comprises a polypropylene film.

15. The container of claim 10 wherein the panel means comprises a uniaxially oriented polymer film comprised of approximately 36% to 60% by weight of polyolefin polymer and 36% to 60% by weight of calcium carbonate based on the weight of the polymer and calcium carbonate.

16. The container of claim 10 wherein the coating means comprises an acrylic polymer.

17. The container of claim 10 wherein the coating means is selected from the group consisting of acrylic polymers, polyvinylacetate or nitrocellulose.

18. The container of claim 10 wherein the coating means is applied to the panel means using a flexographic process.

19. The container of claim 16 wherein the coating means is applied to the panel means using a flexographic process.

20. The container of claim 10 wherein the coating means is applied to the panel means using a rotogravure process.

21. The container of claim 16 wherein the coating means is applied to the panel means using a rotogravure process.

22. The container of claim 15 wherein the polyolefin polymer comprises a propylene homopolymer.

23. The container of claim 15 wherein the polyolefin polymer comprises a propylene/ethylene copolymer.

24. A container for retarding the maturation of respiring items comprising:

package means for substantially surrounding a respiring item and holding the respiring item in an internal chamber formed by the package means, the package means being comprised of a material that is essentially impermeable to oxygen and carbon dioxide;

at least one panel means attached to said package means for providing a limited flow of carbon dioxide and oxygen between said internal chamber and the ambient atmosphere and being comprised of a calcium carbonate-filled uniaxially oriented polymer film comprised of 36% to 60% by weight of polyolefin polymer and 36% to 60% by weight of calcium carbonate based on the weight of the polymer and calcium carbonate, and having a permeance to oxygen in the range of approximately 5,000 to 30,000,000 cc/100 in^2-atmosphere-day; and

a coating means applied to said panel means for decreasing the permeance of said panel means to oxygen or carbon dioxide by more than fifteen percent and comprised of an acrylic polymer.

25. The container of claim 24 wherein the polyolefin polymer comprises a propylene homopolymer.

26. The container of claim 24 wherein the polyolefin polymer comprises a propylene/ethylene copolymer.

27. The container of claim 10 wherein the coating means is applied to the panel means using a rotary silkscreen process.

28. The container of claim 16 wherein the coating means is applied to the panel means using a rotary silkscreen process.

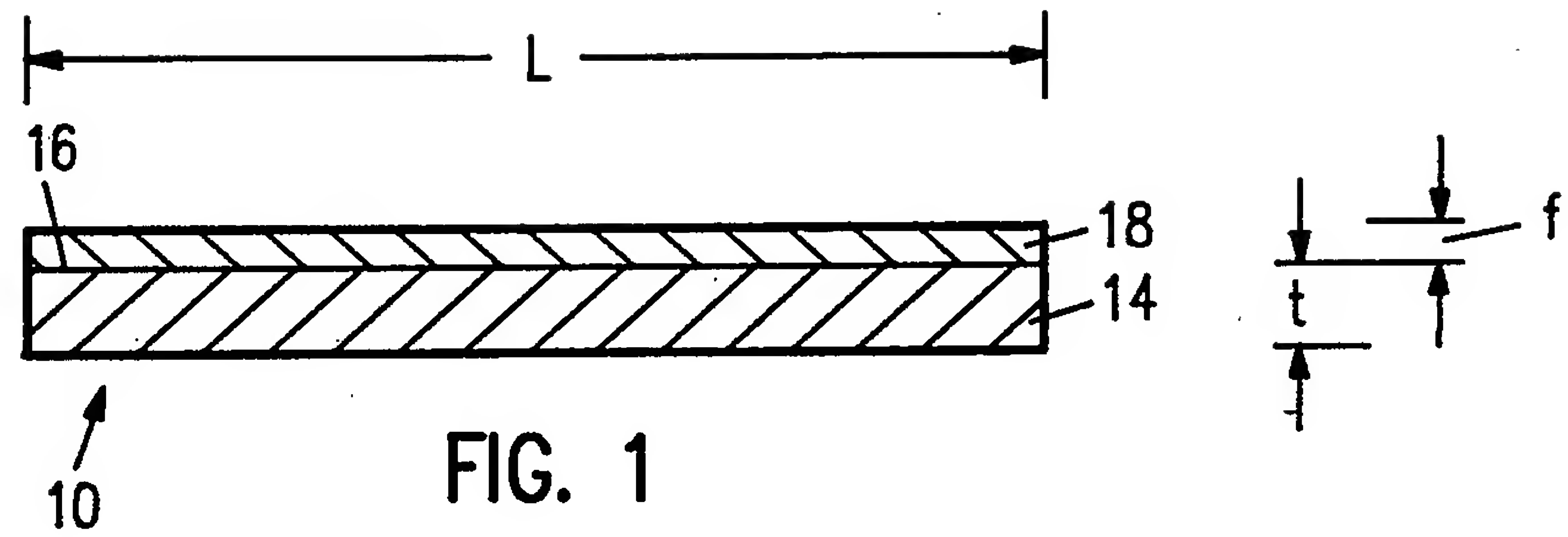


FIG. 1

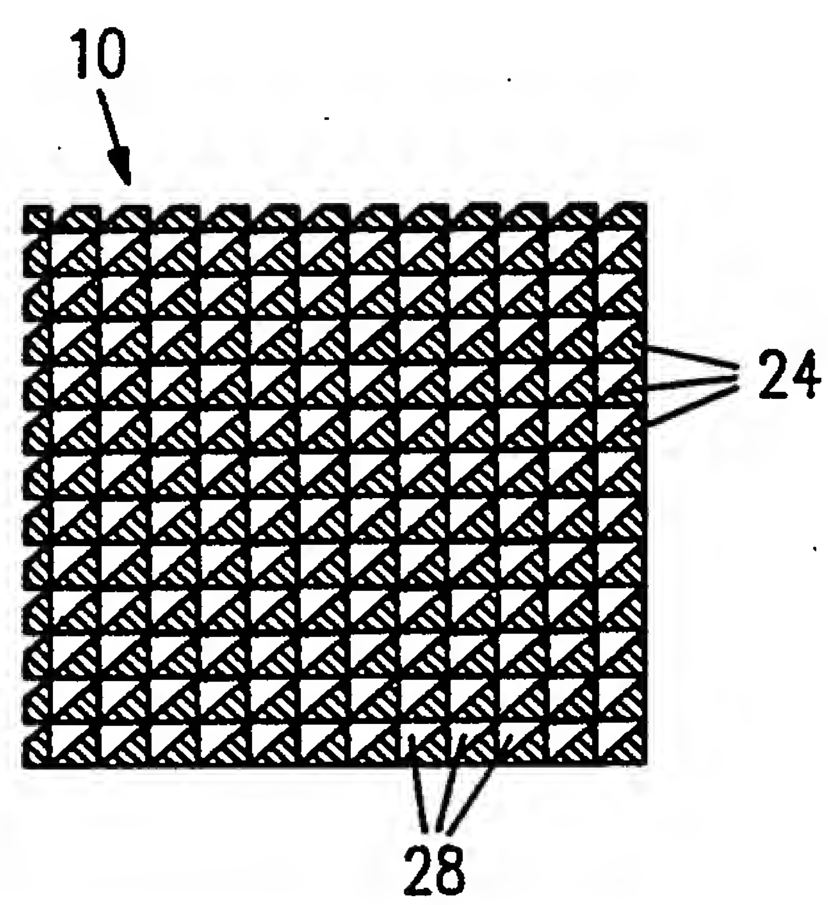


FIG. 2

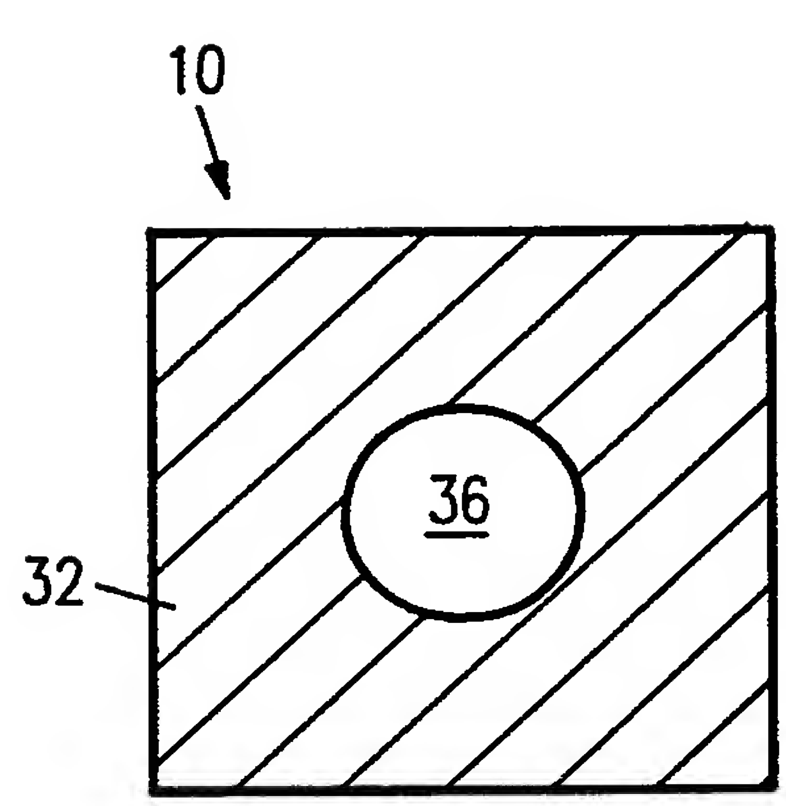


FIG. 3

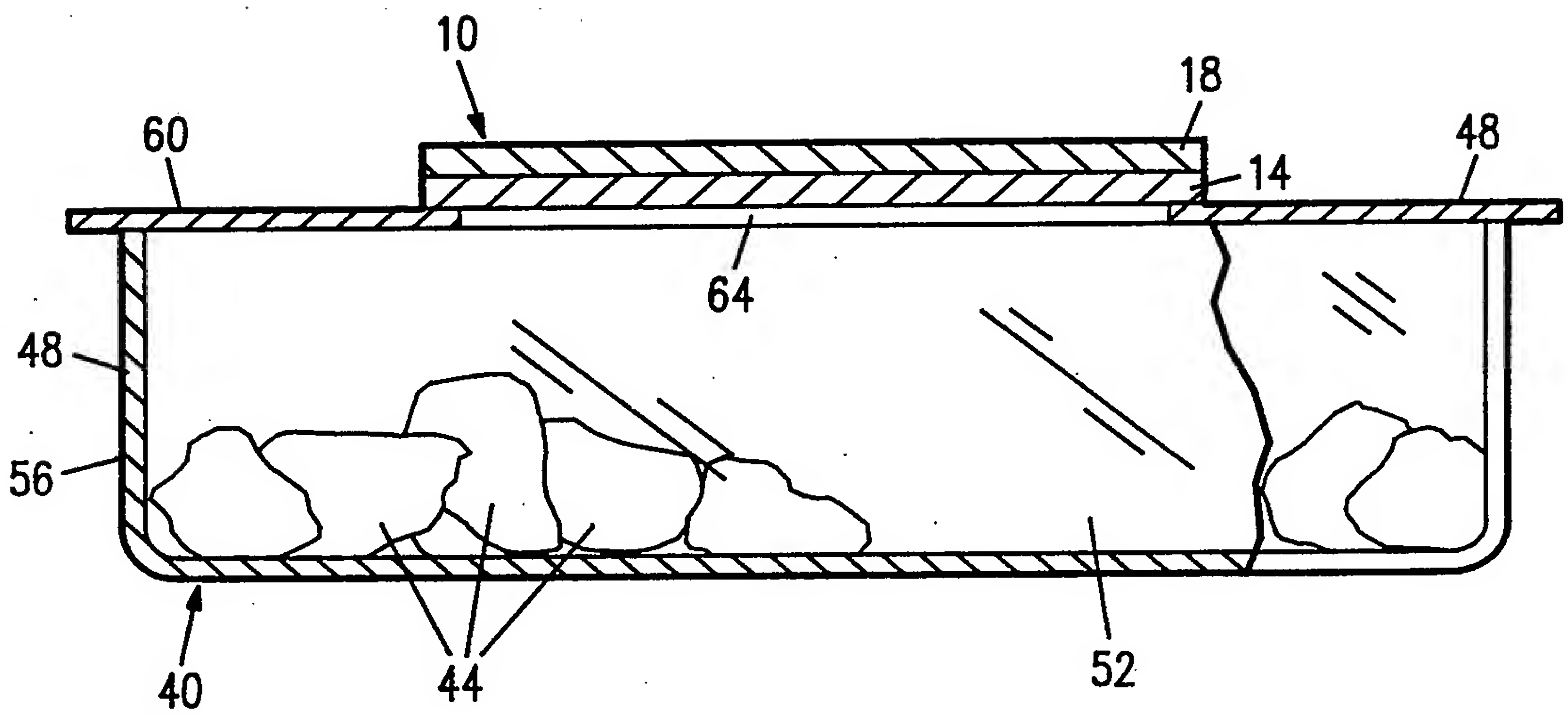


FIG. 4

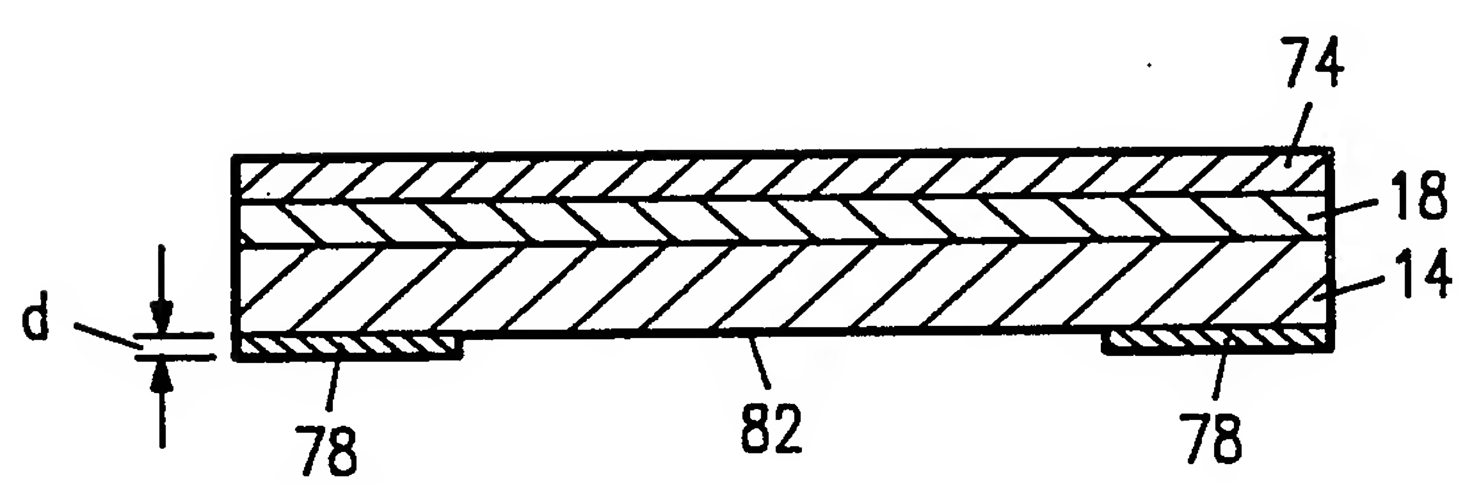


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10669

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :A23B 7/00, B65D 51/16
US CL :220/373; 426/118, 395, 419
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 220/373; 426/118, 395, 415, 419

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,910,032 (Antoon, Jr.) 20 March 1990, col. 2, lines 47-64	1-28
Y	US, A, 4,939,030 (Tsuji et al) 03 July 1990, col.6, lines 5-25.	1-28

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be part of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 January 1994	18 JAN 1994

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Sheila Veney for STEPHEN P. GARBE
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-1207